

DEVELOPMENT OF AN ADVANCED ZINC PHOSPHATE METAL PRETREATMENT

By

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**ABSTRACT**

A SERDP-sponsored program aims at developing environmentally benign zinc phosphate conversion coatings and their process technologies for the electrogalvanized steel (EGS). We succeeded in formulating an environmentally acceptable phosphate solution without Co- and Ni-related additives, and also in replacing a hexavalent Cr acid sealant applied over the zinc phosphate (Zn@Ph) layers with a water-based polysiloxane sealer. The specific advantages of the newly developed Zn@Ph coatings were as follows: 1) there was rapid growth of uniform, dense embryonic Zn@Ph crystals on the EGS surfaces due to the creation of short-circuited cells with Mn acting as the cathode and the galvanized (zinc) coatings as the anode, 2) an excellent protection layer against corrosion was formed, extending the service life of zinc layers as galvanic sacrifice barriers, and 3) adhesion to the electro-deposited polymeric primer coating was improved because of the interaction between the siloxane sealer and primer. A full-scale demonstration to evaluate the reproducibility of this new coating technology on mini-sized automotive door panels made from EGS was carried out in collaboration with the Palmut Company (as industrial coating applicator) in New Jersey. All of the 150 mini-door panels were successfully coated with Zn@Ph.

**1. Introduction**

In the previous SERDP-sponsored program aimed at developing environmentally benign zinc phosphate conversion coatings and their process technologies for cold-rolled steel (CRS) substrates [1], we succeeded in formulating an environmentally-acceptable phosphating solution without Co- and Ni-related additives. The basic formulation consisted of 5 wt%  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , 10 wt% (86 %  $\text{H}_3\text{PO}_4$ ), 3 wt% poly(acrylic acid) [p(AA)] and 82 wt% water; appropriate amounts of the  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  as additives were incorporated into this basic formulation. These additives had two important functions; one was to create a large number of nucleated sites of embryonic Zn@Ph crystals on the steel surfaces, and the other was to act as an inhibitor of corrosion. The p(AA)-modified Zn@Ph coatings not only displayed an excellent salt-spray resistance of > 1000 hrs, but also showed a strong electrochemical affinity with the electro-deposited polymeric primer coatings.

**2. Experimental Details****2.1 Materials**

The metal substrate used was ASE 1006 cold-rolled steel coated with electroplated zinc (EGS, Ford E 60 Electroline 600), supplied by Advanced Coating Technologies, Inc. The formulation for the basic zinc-phosphate liquid

was 5.0 wt% zinc orthophosphate dihydrate (Alfa Co.), 10.0 wt%  $H_2PO_4$ , 1.0 wt%  $Mn(NO_3)_2 \cdot 6H_2O$  (Alfa Co.) and 84.0 wt% water. A water-based polysiloxane sealant, 3-aminopropyltrimethoxy-silane (APS) monomer was supplied. The APS precursor sealant consisted of a 7 wt% APS, 3 wt% methyl alcohol, 0.7 wt% hydrochloric acid and 89.3 wt% water, and had a pH of 9.96. In preparing the polymeric primer coating, all the APS-sealed Zn@Ph panels were coated with the polyurethane-modified epoxy copolymer (POWERCRON 64H) by electrodeposition technology at Advanced Coating Technologies, Inc. The polymeric primer was cured in an oven at 177°C for 30 min.

## 2.2 Measurements

Scanning electron microscopy (SEM) was used to investigate the degree of coverage of the EGS surfaces by p(AA)-modified Zn@Ph coatings and explore the alteration in morphological feature of crystalline Zn@Ph coatings as a function of immersion time. The surface chemical states and phase identification of the coating were carried out using x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD). The concentration of zinc ions dissociated from the EGS surfaces in single  $H_2PO_4$  and  $Mn(NO_3)_2 \cdot 6H_2O$  aqueous solutions, and in their combined medium was determined by atomic absorption spectrophotometry (AA).

DC potentiodynamic polarization measurement for data on the rate of corrosion. The tests were conducted in an aerated 0.5 M NaCl solution at 25°C, on an exposed surface area of 1.0 cm<sup>2</sup>. AC electrochemical impedance spectroscopy (EIS) was used to evaluate the ability of coating films to protect the EGS from corrosion. Specimens with a surface area of 13 cm<sup>2</sup> were exposed to an aerated 0.5 N NaCl electrolyte at 25°C, and single-sine technology with an input AC voltage of 10 mV (rms) was used over a frequency range of 10 kHz to 2 MHz. The salt-spray tests for the primed Zn@Ph coating panels were carried out in accordance with ASTM D1654-79a.

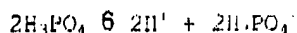
## 3. Results and Discussion

### 3.1 p(AA)-Modified Zn@Ph Coatings on EGS

Figure 1 shows SEM micrographs of crystalline Zn@Ph coatings derived from the p(AA)-modified phosphating solutions as a function of the immersion time of the EGS substrate into the phosphating bath at 80°C. Immersion for 5 sec was sufficient to produce dense conversion coatings over the entire substrate surface (see Fig. 1-c). A immersing time to 10 sec (d) revealed a densely packed conformation of lamellar Zn@Ph crystals, reflecting that the EGS surface had essentially been altered and now had a rough microstructure.

Figures 2 and 3 show the high-resolution XPS spectra of  $P_{2p}$ ,  $Zn_{2p_{3/2}}$ , and  $C_{1s}$  core-level excitations for the Zn@Ph coatings as a function of treatment time. Because the peak at 1023.0 eV belongs to Zn originating from Zn@Ph [8], this result strongly supported the SEM data showing that an immersion of 5 sec is long enough to cover the whole surface of EGS with Zn@Ph. An important question remains to be solved: namely, why the  $Mn(NO_3)_2 \cdot 6H_2O$ -incorporated solution causes the rapid deposition of Zn@Ph on the EGS surfaces.

$Mn(NO_3)_2 \cdot 6H_2O$  solution,  $2.7 \times 10^{-4}$  g/ml of Zn ions dissociate from the EGS surfaces in the first 2 sec of immersion; thereafter, the rate of Zn ion dissolution increases with increased time Figure 4. These findings verified that the addition of  $Mn(NO_3)_2 \cdot 6H_2O$  to  $H_3PO_4$  solution significantly promotes the dissolution of Zn ions from the EGS surfaces in conjunction with a more brisk evolution of hydrogen with Zn acting as the anodic area and Mn as the cathode. Mn side:



From this information, we show the hypothetical conversion mechanisms of Mn-incorporated  $H_3PO_4$  solution into zinc phosphate phase over the EGS (Fig 5). Figure 6 illustrates the XRD tracing, ranging from 0.444 to 0.225 nm, of the "as-received" EGS as a control, and the p(AA)-modified Zn@Ph coatings prepared by immersing EGS panels for 1, 2, 5, and 10 sec.

### 3.2 Water-Based APS Sealant

All Zn@Ph coatings contain some voids remain in the coating layers. These must be filled for maximum corrosion protection. The goal of this part of the research was on the non-toxic, water-based APS sealant used to replace the conventional toxic hexavalent chromic acid as corrosion-inhibiting sealant.

In the XPS study earlier, we found that the p(AA) polymers remain at the outermost surface sites of Zn@Ph layers. Thus, it is very important to know how the APS sealer reacts with the p(AA) polymers chemisorbed to the Zn@Ph. The results strongly demonstrated that when the APS was attached to the p(AA), the  $NH_2$  groups in APS favorably reacted with the carboxyl in p(AA) to form the amide bonds. Thus, it is conceivable that the formation of interfacial amide bonds acts to link strongly p(AA) to the APS films and are illustrated in Fig A.

Figure 7 depicts typical polarization curves log current versus potential for the uncoated EGS, and Zn@Ph- and p(AA)-Zn@Ph-coated EGS panels. When compared with those for the uncoated EGS, the form of the cathodic curves for

the coated EGS specimens are as follows: (1) a decreased current in the vicinity of  $E_{\text{corr}}$ , and (2) a lower short-term steady-state current value in the potential region between -1.2 and -1.0 V. As a result, it appears that the ability of zinc layers in the EGS to inhibit the cathodic reaction in terms of the oxygen reduction reaction,  $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$ , of the underlying steel was further enhanced by the p(AA)-modified and unmodified Zn@Ph coatings. Thus, we believe that the formation of interfacial amide bonds by the interaction between APS and p(AA) significantly contributes to protecting steel from the corrosion, suggesting that the APS has a high potential for use as sealer of the p(AA)-modified Zn@Ph coatings.

Based upon these polarization curves **Figure 8**, we attempted to determine the absolute corrosion rates of steel, expressed in the conventional engineering units of milli-inches per year (mpy). The equation (1) proposed by Stern and Gery [19], was used in the first step:

$$I_{\text{corr}} = \frac{I_a @ E_c}{2.303 (\eta_a + \eta_c)} R_p \quad (1)$$

where  $I_{\text{corr}}$  is the corrosion current density in A,  $\eta_a$  and  $\eta_c$  having the units of volts/decade of current refer to the anodic and cathodic Tafel slopes.

**Table 1** gives the  $I_{\text{corr}}$  and corrosion rate obtained from this Tafel calculation for various coating panels. A significant decrease in corrosion rate can be seen from the APS-sealed panels, especially in the APS/p(AA)-Zn@Ph coating system. The rate of 0.022 mpy for this coating system was approximately two orders of magnitude less than that of the uncoated EGS.

In support, all the test panels were exposed in a 5 % salt fog chamber at 35°C to determine the extension of useful lifetime of the coatings that protect the zinc layer in EGS against white rusting. The results from these test panels are shown in **Table 2**.

### 3.3 Electrically Deposited Primer Coatings

We verified that the APS sealed Zinc Phosphate surface could be E-Coated. We did this using PPG's Powercron 648 chemistry **Figure B**. To gain this information, we electrically deposited the primer coatings onto the APS-sealed and unsealed Zn@Ph layers, and then examined the ability of primer coatings to further improve the protection of EGS against corrosion by AC electrochemical impedance spectroscopy (EIS) and the 5 % salt-spray tests.

Six different coating systems, electrically deposited primer (EDP), EDP/Zn@Ph, EDP/p(AA)-Zn@Ph, EDP/APS, EDP/APS/Zn@Ph, and EDP/APS/p(AA)-Zn@Ph, were prepared for this examination.

In the EIS tests, the curves (not shown) for all the coated EGS panels depicted the Bode-plot features [the absolute value of impedance  $|Z^*|$  (ohm-cm<sup>2</sup>) vs. frequency (Hz)]. This information was correlated directly with the states

of primer-coated panels after salt-spray tests for 1080 hours. The results from these test panels are shown in Table 3.

### 3.4 Industrial-Scale Demonstration Tests

To demonstrate the reproducibility of this coating technology on mini-sized automobile door panels made from EGS, a full-scale feasibility test was carried out in collaboration with the Palnut Company, NJ. Coating involved the cleaning, coating, rinsing, sealing, and drying (Fig. 10). The four separate solution tanks with a 1514 L (400 Gal.) were used. To ensure that this coating process was reproducible, the procedure was repeated ten times; all 150 mini-sized door panels were successfully coated with Zn@Ph.

### 4. Conclusions

We modified the surface of electrogalvanized steels (EGS) to inhibit corrosion of Zn layers and to improve their sealer-adhesion properties by immersing EGS panels into environmentally acceptable zinc phosphating solutions consisting of  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$ , poly(acrylic acid) [p(AA)],  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and water at 80°C. The electrochemical reaction between Mn dissociated from  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and Zn in the acid media created short-circuited cells by the flow of electrons from Zn acting as the anode to Mn on the cathode. Uniform hopeite layers completely converting over the EGS surfaces were observed on the specimens prepared by immersion for only 5 sec, thereby conferring good protection layers against corrosion. Hexavalent Cr acids known to be environmental hazards are commonly used as a sealant for the Zn@Ph layers because they improve the ability of Zn@Ph to protect the metal from corrosion. Hence, our attention was paid to find the replacing materials for the Cr acids. We succeeded in developing an environmentally acceptable water-based 3-aminopropyltrimethoxysilane (APS) sealant. In addition, the APS sealer had a strong chemical affinity for the polyurethane-modified epoxy primer coating induced by the electrodeposition technology. We concluded this test by running a scale up demonstration at the Palnut Company, using a 400-gallon industrial size tank. In all 150 panels were successfully coated with APS-sealed Zn@Ph.

### 5. Recommendations

1. The optimum formulation for an environmentally benign zinc phosphating solution suitable for (EGS) was 5 wt%  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  powder, 10 wt% 85%  $\text{H}_3\text{PO}_4$ , 1.0 wt%  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and 84 wt% water, in conjunction with poly(acrylic acid) [p(AA), M.W. 60,000] additive of 3.0 wt% by total weight of basic zinc phosphating solution.

2. The water-based 3-aminopropyltrimethoxysilane (APS) sealant consisting of a 7 wt% APS, 3 wt% methyl alcohol, 0.7 wt% hydrochloric acid, and 89.3 wt% water, can be used to replace the conventional hexavalent Cr acid sealant.
3. Using the process technology developed in this work, the p(AA)-modified zinc phosphate (Zn@Ph) conversion coatings with a APS sealer were prepared in accordance with the following sequence: 1) pickling the EGS panels in a 2 wt%  $H_3PO_4$ -1 wt%  $H_2SO_4$ -97 wt% water solution for 1 min at 25EC, 2) immersing the surfaces-cleaned EGS panels for 1 min into the p(AA)-dissolved zinc phosphate solution at 80EC, 3) rinsing the Zn@Ph-coated EGS surfaces with water, 4) dipping the water-rinsed Zn@Ph coating panels for few seconds into a 7 wt% APS sealing agent at 25EC, and 5) drying the APS-wetted Zn@Ph coating panels for 30 min in an oven at 150EC.
4. Conduct a long-term exposure in a corrosive environment to ensure that they afford an adequate protection of EGS against corrosion.

#### 6. Acknowledgments

The authors are grateful to Dr. Robert K. Reeber, U.S. Army Research Office (ARO), for his invaluable suggestions; and to Dr. Joseph Lucas, PPC Industries, Inc., for his assistance to prepare electrodeposited topcoatings on the Zn@Ph surfaces. Discussions with Mr. Philip H. Austin, the Palnut Company, is also appreciated.

**Table 1. Tafel Analyses for Polarization Curves of Coated EGS Panels**

Coating	$E_{corr}(I=0)$ V	$\beta_a$ V/decade	$\beta_c$ V/decade	$I_{corr}$ A	Corrosion rate mpy
Uncoated	-0.8711	0.0669	0.1513	$3.17 \times 10^{-6}$	1.449
Zn@Ph	-0.9692	0.0472	0.1660	$1.11 \times 10^{-6}$	0.505
p(AA)-Zn@Ph	-0.9609	0.0668	0.1547	$1.03 \times 10^{-6}$	0.467
APS	-0.8293	0.0458	0.1312	$3.10 \times 10^{-7}$	0.142
APS/Zn@Ph	-0.8453	0.0532	0.1227	$2.12 \times 10^{-7}$	0.097
APS/p(AA)-Zn@Ph	-0.8421	0.1257	0.1634	$4.78 \times 10^{-8}$	0.022

**Table 2. Salt-Spray Resistance of Coated EGS Panels**

Coating	Salt-spray resistance Hr
Uncoated	15
Zn@Ph	190
p(AA)-Zn@Ph	264
APS	340
APS/Zn@Ph	612
APS/p(AA)-Zn@Ph	750

**Table 3. Evaluation of EDP-Coated EGS Panels Subjected to 5% Salt Spray Testing**

Coating	Exposure hr	Representative mean creepage from scribe mm	Area of blister formed in inscribed areas %
EDP	360	10.0	.80
EDP/Zn@Ph	1080	8.5	.32
EDP/p(AA)-Zn@Ph	1080	6.5	.28
EDP/APS	1080	3.0	.20
EDP/APS/Zn@Ph	1080	1.8	.13
EDP/APS/p(AA)- Zn@Ph	1080	1.2	.5

**Figure 10**

1. Pickled (2 wt%  $H_3PO_4$ -1 wt%  $H_2SO_4$ -97 wt% water) for 1 min at 25°C
2. Immersed in zinc phosphate solution for 1 min at 80°C
3. Rinsed with water
4. Dipped in water-based polysiloxane sealant
5. Oven-dried for 30 min at 150°C
6. Electrodeposited primer coatings

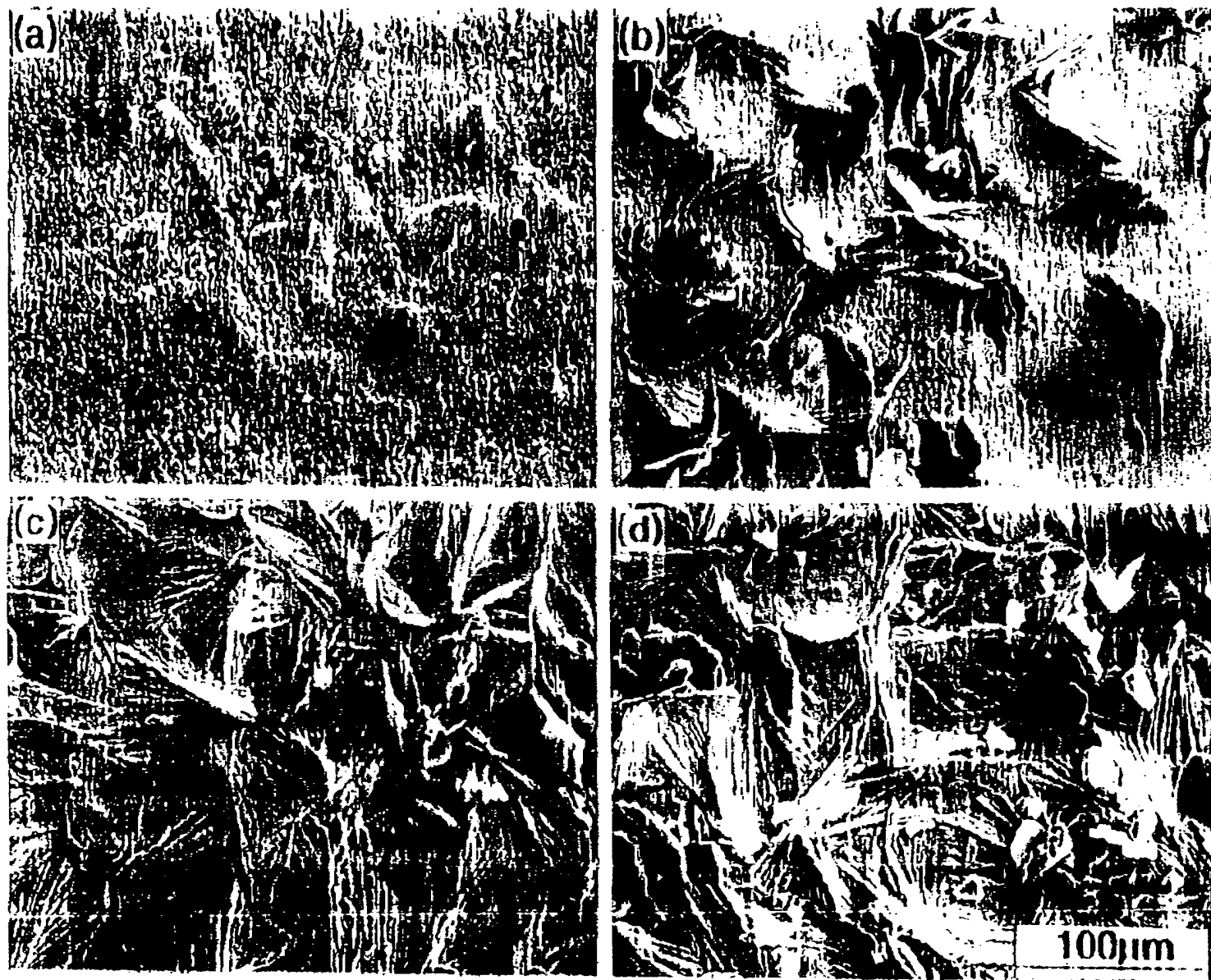


Figure 1 SEM Image of (GAA) modified surfaces after immersion for 1 sec (a), 2 sec (b), 5 sec (c), and 10 sec (d)

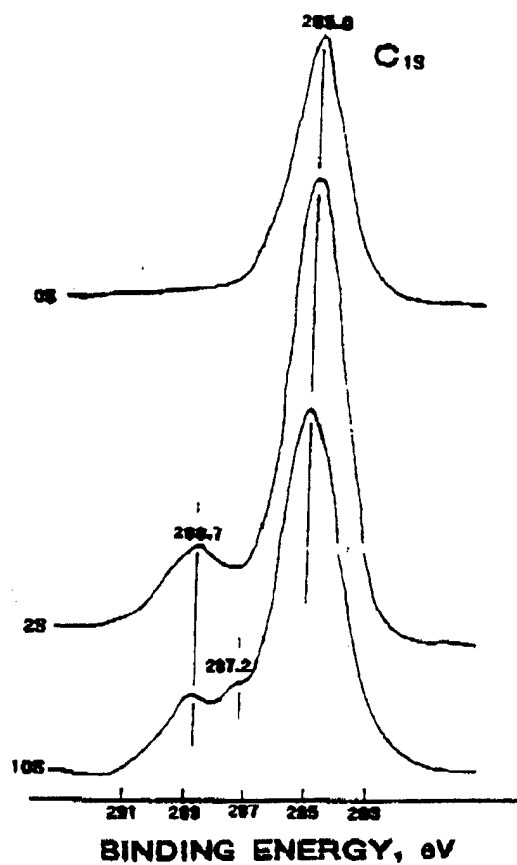


Figure 3. C<sub>1s</sub> region of "as-received" EGS (OS), and 2s and 10s-treated Zn·Ph surfaces.

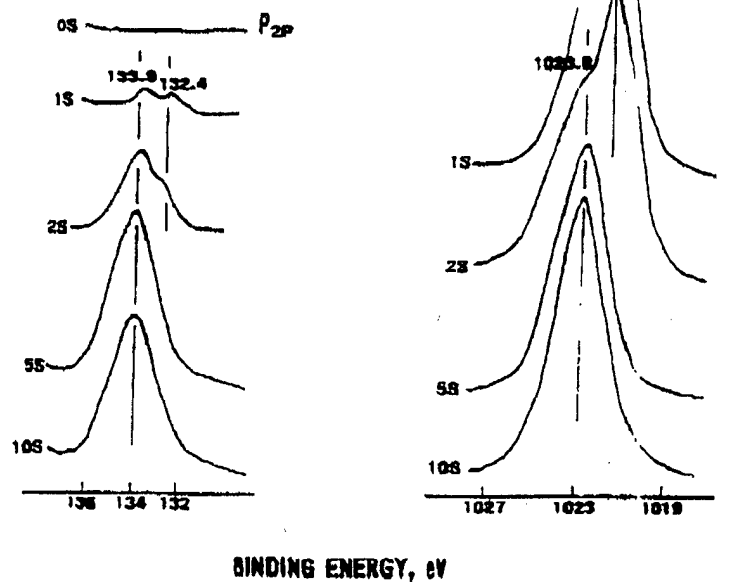


Figure 2. XPS P<sub>2p</sub> and Zn<sub>2p<sub>3/2</sub></sub> regions of Zn·Ph deposited on EGS as a function of immersion time.

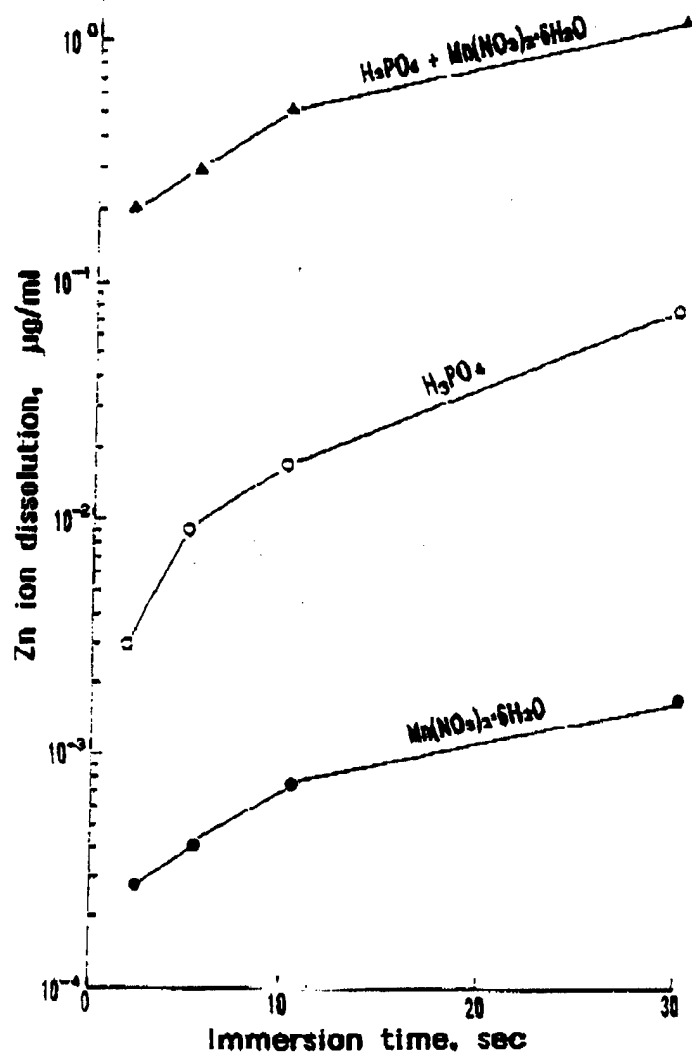


Figure 6. Changes in the concentration of zinc ions dissolved anodically from galvanized coating after immersion of ECS into  $H_3PO_4$ ,  $Mn(NO_3)_2 \cdot 6H_2O$ , and  $H_3PO_4 + Mn(NO_3)_2 \cdot 6H_2O$  solution, respectively, at 80°C.

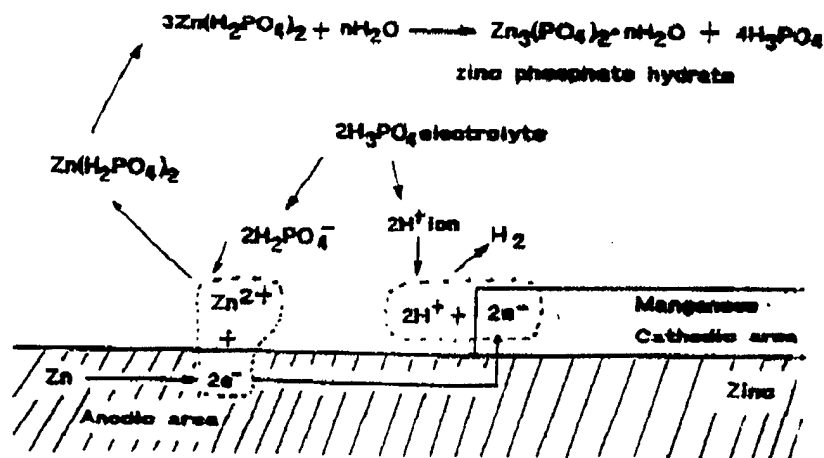


Figure 5. Hypothetical multiple reactions occurring at interfaces between ECS and Mn-incorporated  $H_3PO_4$  electrolyte.

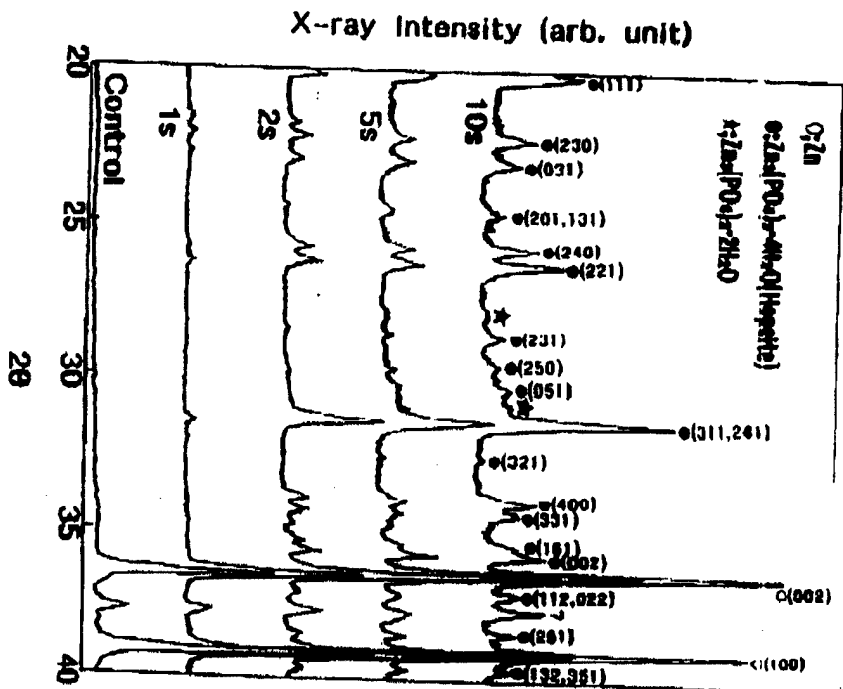


Figure 6. XRD patterns of "as-received" EGS surfaces as control, and Zn-Rh made after immersion for 1, 2, 5, and 10s.

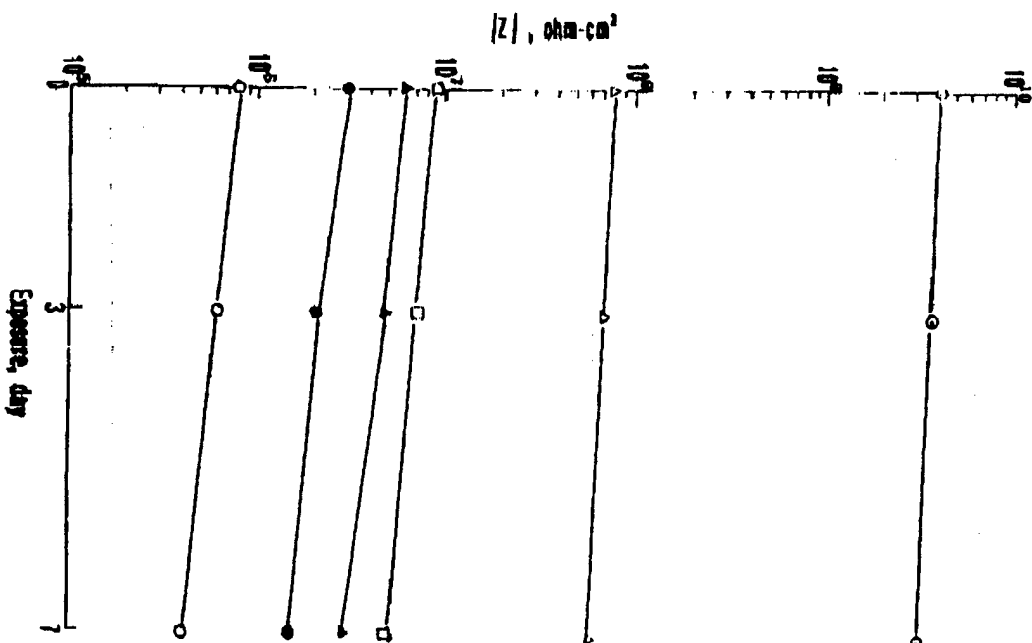


Figure 9. Changes in impedance value for (0) EDP-Zn-Rh, (1) EDP/APS-Zn-Rh, (2) EDP/APS/Zn-Rh, and (3) EDP/APS/p(AM)-Zn-Rh-coated EGS panels as a function of exposure time.

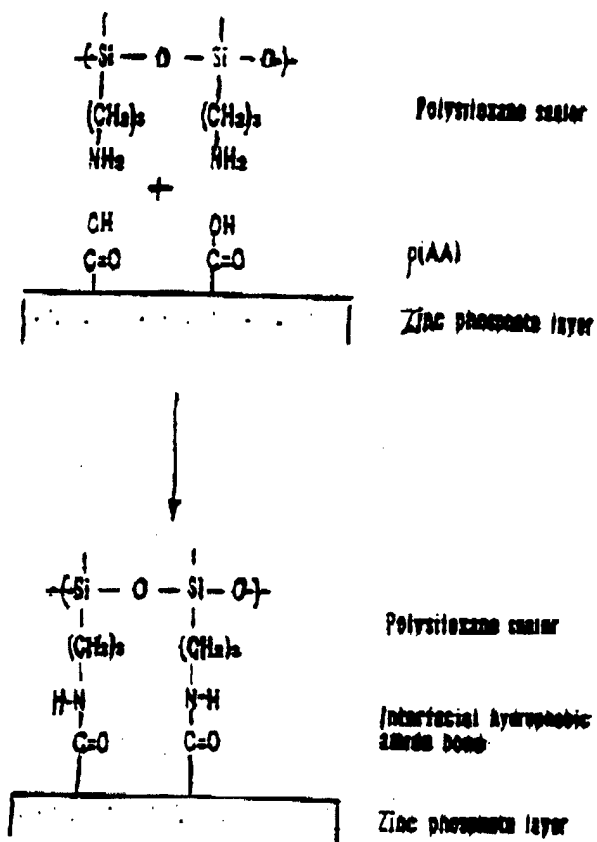


Figure A

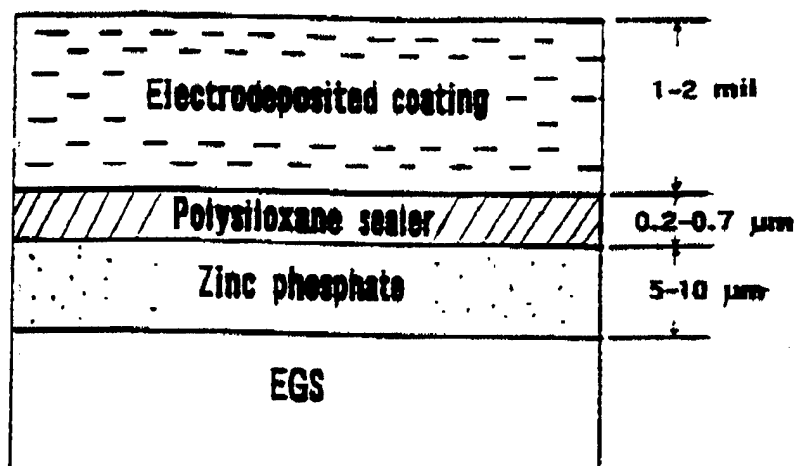


Figure B

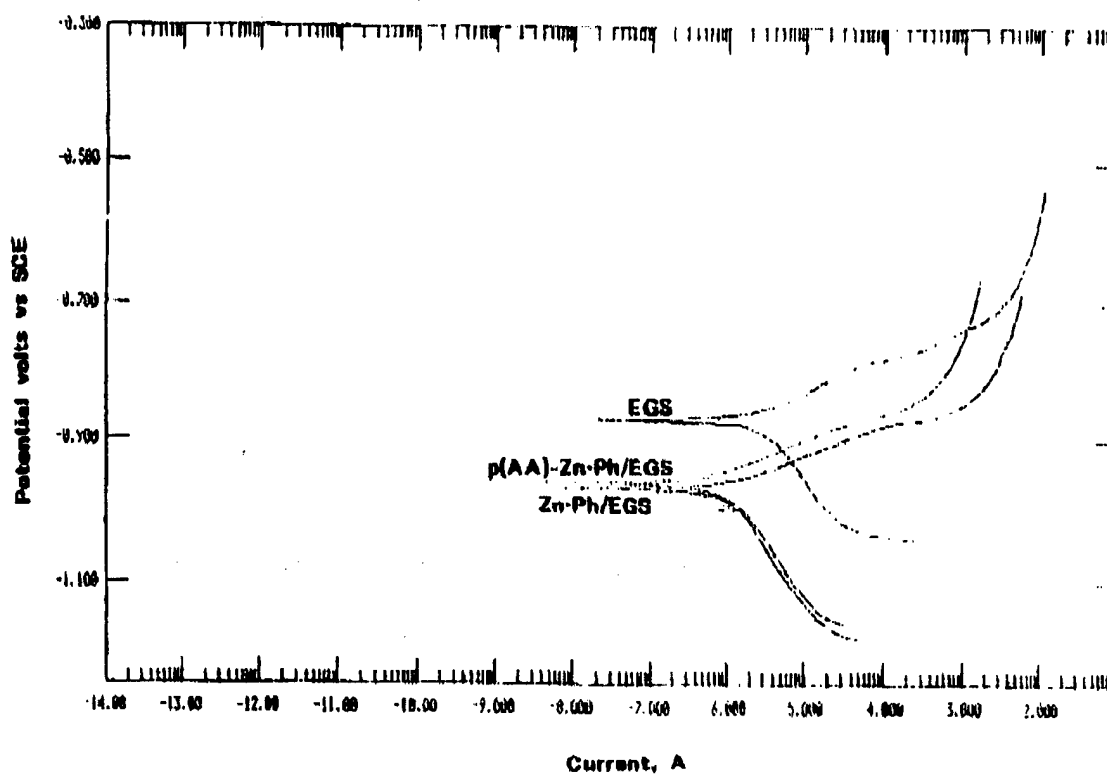


Figure 7. Polarization curves for "as-received" EGS, and p(AA)-modified and unmodified Zn-Ph coating panel

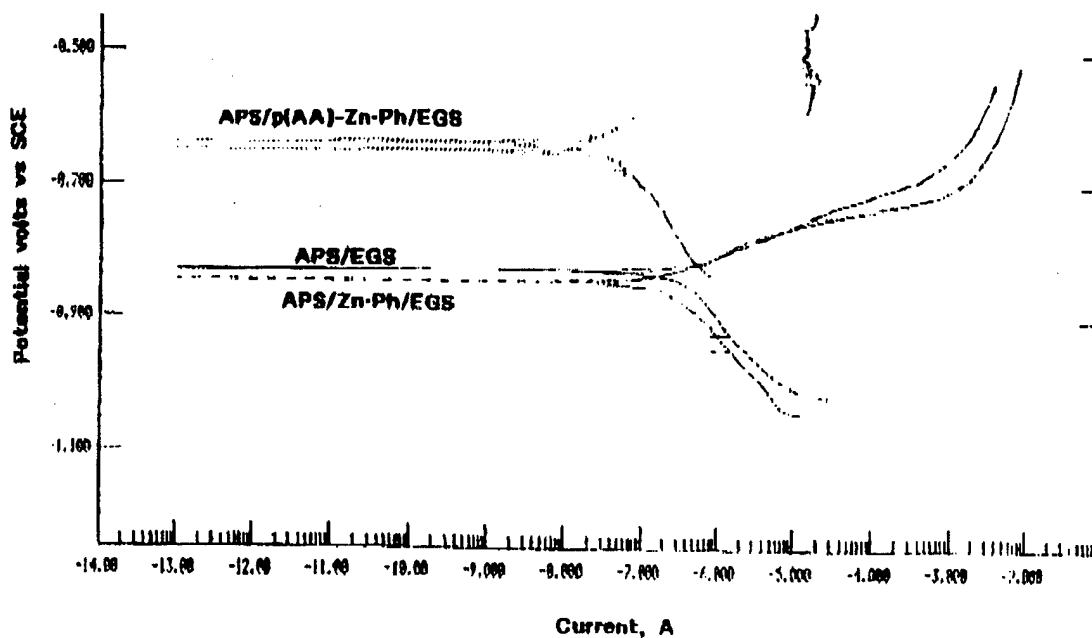


Figure 8. Polarization curves for the APS-sealed EGS, Zn-Ph, and p(AA)-Zn-Ph panels.